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A2

WO 2004/050955

(54) Title: SEPARATION OF METALS

(57) Abstract: The invention provides a process for the separation of metals, the metals being comprised as the metal oxides in a mixed oxide sample, the process comprising: (i) adding the mixed oxide to a molten salt electrolyte and cathodically electrolysing the oxide, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of metal from the cations present in the molten salt, and the applied potential difference being such as to facilitate selective reduction of one metal oxide at the expense of other metal oxides; and (ii) separating the metal from the remaining metal oxides, wherein the metal oxides comprise oxides of metals from at least one of the transition metal, lanthanide or actinide series. The process is applicable to mixed oxide samples comprising mixtures of two or more metal oxides, and a particular application is in the separation of zirconium and hafnium comprised in mixed zirconium and hafnium oxides, the removal of hafnium facilitating the use of the zirconium in fuel cladding for use in the nuclear power industry.

SEPARATION OF METALS

Field of the Invention

This invention relates to a method for the separation of metals from mixtures of metal oxides and relies on the selective reduction of certain oxides to the metals, whilst the other metals remain in the form of the oxides. The method of the present invention finds particular application in the separation of transition metals, lanthanides and actinides.

10 Background to the Invention

The prior art teaches the use of molten salts in the separation of metals and metal oxides in molten salt media. As used herein, the term "molten salts" is intended to cover salts such as lithium chloride which melts at an elevated temperature and also ionic liquids which typically are liquid at room temperature or which melt at a temperature up to about 300°C. Such techniques have found particular application in the nuclear industry, where two well-established processes are available for the treatment of irradiated nuclear fuel.

The first of these processes, the Dimitrovgrad SSC-RIAR process, makes use of 20 chemical oxidants (chlorine and oxygen gases) to react with powdered uranium dioxide fuel to form higher oxidation state compounds such as UO_2Cl_2 which are soluble in the molten salt. In an electrochemical cell the uranium compounds are reduced to UO_2 at the cathode, forming a solid deposit. This process has both technical and environmental limitations.

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The second process, developed by the Argonne National Laboratory (ANL) is fundamentally an electrorefining technology which uses current flow to anodically oxidise uranium to form uranium ions in the molten salt electrolyte. At the cathode the uranium is reduced and electrodeposited as uranium metal.

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The ANL process requires a metal feed. If oxide fuels are to be treated, it is necessary to reduce the uranium oxide (usually UO₂ pellets) to the metal. This reduction process is carried out chemically, using lithium metal in a LiCl or LiCl/KCl molten salt at 500 to 600°C. Alternatively, a salt transport process can be used 5 involving a Cu-Mg-Ca alloy and molten CaCl₂ salt. However, in both reduction methods the by-products, Li₂O and CaO respectively, need to be recovered from the molten salt phase by an electrolysis step. Effectively this means a two stage process.

A disadvantage of the lithium reduction process for producing a metallic feed from 10 an oxide is the production of Li₂O by-product. This requires recycle to make the process economic, and this is done by an electrolytic recovery of lithium metal. Hence this is a two stage process, comprising a reduction step followed by a lithium recovery stage.

15 More recently, in EP-A-1088113, there is proposed a method for the removal of oxygen from a metal oxide wherein an electrode comprising the metal oxide is contacted with a molten salt, and a potential is applied which is lower than the deposition potential of the cation of the molten salt, thereby facilitating removal of oxygen from the metal oxide.

20 Subsequently, in the PCT patent application published under No WO-A-01/41152, there is disclosed a single step process for reducing to metallic form a metal oxide present in spent nuclear fuel, the process comprising cathodically electrolysing the oxide in the presence of a molten salt electrolyte, the potential of the cathode being 25 controlled so as to favour oxygen ionisation over deposition of the metal from the cations present in the molten salt.

30 The process thereby involves the use of a single electrochemical process to reduce the metal oxide fuel to a metallic form, with oxygen, carbon monoxide and carbon dioxide produced as the only by-products. The potential of the cathode is maintained and controlled so that only oxygen ionisation occurs and not the deposition of the

cations (eg Ca ions) in the fused salt. Typically, the oxide comprises an actinide oxide, such as uranium oxide or irradiated uranium oxide.

This process was then developed and applied to the separation of metals from a mixture of metal oxides such as occurs in spent nuclear fuel, which is a frequent requirement in the nuclear power industry. Thus mixtures of uranium and plutonium oxides, together with the oxides of other actinide metals, may additionally be contaminated with oxides of other, chemically active, metals such as, for example, those associated with fission products. Co-pending patent application No PCT/GB02/02402 teaches a method for the treatment of irradiated fuel which allows for the separation of uranium, and metals more noble than uranium, from such mixtures as are found in spent nuclear fuel, and facilitates the provision of these metals in a form suitable for use as the feed in a molten salt electrorefining process, whilst ensuring that other, more electropositive, metals remain in the form of oxides.

The present inventors, however, recognised that there is frequently the requirement, both within the nuclear industry and the wider chemical industry, for the separation of metals from mixtures of metal oxides, and that the established technologies within these industries often provide inadequate means for the performance of such separations. Thus, whilst the prior art, as previously discussed, has focused largely on applications within the nuclear power industry and, most particularly, on processes involving actinide metals, it is often necessary, in a wide range of industries, to separate a large variety of metals, many of which are not members of the actinide series.

The present invention, therefore seeks to provide a method for the electrochemical separation of metals, the method relying on the different reduction potentials of different oxides which results in the reduction of one oxide to the free metal, whilst the other metal remains as the oxide. Examples of metals which might be separated in this way include transition metals, lanthanides and actinides.

Statements of Invention

Thus, according to the present invention, there is provided a process for the separation of metals, said metals being comprised as the metal oxides in a mixed oxide sample, the process comprising:

- 5 (i) adding the mixed oxide to a molten salt electrolyte and cathodically electrolysing the oxide, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of metal from the cations present in the molten salt, and the applied potential difference being such as to facilitate selective reduction of one metal oxide at the expense of other metal oxides; and
- 10 (ii) separating the metal from the remaining metal oxides,
wherein the metal oxides wherein comprise oxides of metals from at least one of the transition metal, lanthanide or actinide series.

The potential of the cathode is maintained and controlled so that only oxygen ionisation occurs and not the deposition of the cations (eg Ca ions) in the fused salt, and also to ensure that, whilst reduction of one of the metals occurs smoothly, the other metals are not reduced and remain in the anode as oxides. The only by-products which are produced are oxygen, carbon monoxide and carbon dioxide gases.

- 20 The process may be applied to the separation of a wide variety of metals of the transition, lanthanide and actinide series which are comprised as the oxides in mixed oxide samples. The broad usefulness and versatility of the method is illustrated by its applicability to the separation of metals from mixtures of two or more metal oxides. Thus, it is possible to apply the method of the invention to the separation of metals of the transition, lanthanide and actinide series comprised as the oxides in mixed oxide samples comprising oxides of one, two or three of the said series. In other words, the method of the invention facilitates the separation of metals from mixed oxide samples which comprise any of the following combinations:
 - 25 (a) transition metal oxides only;
 - (b) lanthanide oxides only;
- 30

- (c) actinide oxides only;
- (d) at least one transition metal oxide and at least one lanthanide oxide;
- (e) at least one transition metal oxide and at least one actinide oxide;
- (f) at least one lanthanide oxide and at least one actinide oxide; or
- 5 (g) at least one transition metal oxide and at least one lanthanide oxide and at least one actinide oxide.

A specific example of a preferred application of the process is in the separation of hafnium, present as the oxide, in samples of zirconium oxide. Zirconium metal is
10 widely used in the nuclear power industry in zircaloy cladding. However, hafnium serves as a poison in nuclear reactors and it is vital, therefore, that it should be removed from the zirconium metal prior to the incorporation of this material in cladding. Its removal is facilitated by the process of the present invention, wherein a suitable potential difference is applied in order to facilitate the reduction of
15 zirconium oxide to zirconium metal whilst leaving the hafnium oxide unchanged.

The mixed oxide may be in any physical form, and this is generally dependent on the particular application from which it has resulted. For example, it may be provided as solid pieces of irregular size and shape, but it may also comprise a powder, an
20 amorphous mass, or a dense solid agglomerate. In any event, the material may be treated according to the method of the present invention by connection to an electrical circuit such that it serves as the cathode during electrolysis. Connection to the circuit may be effected by any of the standard means well known to those skilled in the art.

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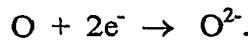
Preferably the mixed oxide is in contact with the cathode of an electrochemical cell. The cathode could be in the form of a mesh basket. The molten salt electrolyte may be any suitable molten salt or mixture of such salts, for instance chloride salts, preferably CaCl_2 and/or BaCl_2 . The anode may be any suitable inert anode, such as
30 carbon.

The separation step, whereby the metal is separated from the remaining metal oxides, may comprise any of a number of techniques well known to those skilled in the art. Thus, for example, simple dissolution and solvent extraction techniques may be applicable; alternatively, heating and slagging methods could be appropriate. As a 5 further alternative, additional electrochemical means may be employed to effect the separation.

Optionally, reduction of the selected metal oxide may be carried out in one particular molten salt, whilst separation of that metal from the other metal oxide or oxides is 10 effected in a different molten salt composition. Alternatively, the two processes may be performed in the same molten salt.

Detailed description of the Invention

In order to carry out an embodiment of the present invention, an electrolytic cell is 15 assembled which has a carbon anode and a mesh basket cathode. A mixed oxide sample is placed in the mesh basket. The electrolyte consists of a molten salt or a mixture of such salts comprising, for example, chloride salts such as CaCl₂ or BaCl₂. A voltage is applied between the cathode and the anode. At the cathode the reaction involves the diffusion of oxygen atoms to the surface of the solid, followed by 20 ionisation according to the reaction:



The oxide ions which are produced dissolve in the electrolyte and are transferred to the anode where they are re-oxidised to produce oxygen gas. Further by-products include carbon monoxide and carbon dioxide. The potential at the cathode may be 25 controlled, via a third reference electrode, to ensure that the reaction occurring at the cathode is oxygen ionisation and not deposition of the cations in the fused salt, and that only a selected metal oxide is reduced. Electrolysis at elevated temperatures results in an increased rate of oxygen diffusion, thereby also encouraging ionisation rather than metal deposition.

After electrolysis the mixed oxide sample is left in the form of a metal/metal oxide solid mixture at the cathode, with one of the metals having been reduced to the metallic form, whilst the other metals remain in the form of their oxides. This metallic/metal oxide product is then subjected to a suitable separation treatment.

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CLAIMS

1. A process for the separation of metals, said metals being comprised as the metal oxides in a mixed oxide sample, the process comprising:
 - 5 (i) adding the mixed oxide to a molten salt electrolyte and cathodically electrolysing the oxide, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of metal from the cations present in the molten salt, and the applied potential difference being such as to facilitate selective reduction of one metal oxide at the expense of other metal oxides; and
 - 10 (ii) separating the metal from the remaining metal oxides.
wherein said metal oxides comprise oxides of metals from at least one of the transition metal, lanthanide or actinide series.
- 15 2. A process as claimed in claim 1 wherein said mixed oxide sample comprises a mixture of two or more metal oxides.
3. A process as claimed in claim 1 or 2 wherein said metals comprise zirconium and hafnium and said mixed oxide sample comprises mixed zirconium and hafnium oxides.
- 20 4. A process as claimed in any one of claims 1 to 3 wherein the mixed oxide is provided as solid pieces of irregular size and shape, a powder, an amorphous mass, or a dense solid agglomerate.
- 25 5. A process as claimed in any preceding claim wherein the oxide is located in a mesh basket which forms the cathode.
- 30 6. A process as claimed in any preceding claim wherein the molten salt electrolyte comprises at least one chloride salt.

7. A process as claimed in claim 6 wherein the chloride salt is CaCl_2 or BaCl_2 .
 8. A process as claimed in any preceding claim wherein the anode is a carbon anode.
- 5
9. A process as claimed in any preceding claim wherein the step of separating the metal from the remaining metal oxides is carried out by the use of dissolution and solvent extraction techniques, heating and slagging methods or electrochemical means.
- 10
10. A process as claimed in any preceding claim wherein said reduction of the selected metal oxide is carried out in one molten salt whilst separation of the metal from the other metal oxide or oxides is effected in a different molten salt composition.
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11. A process as claimed in any one of claims 1 to 9 wherein said reduction of the selected metal oxide and said separation of the metal from the other metal oxide or oxides is performed in the same molten salt.

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(75) Inventors/Applicants (*for US only*): LEWIN, Robert, Glyn [GB/GB]; British Nuclear Fuels plc, Sellafield Works, Seascale, Cumbria CA20 1PG (GB). THIED, Robert, Charles [GB/GB]; British Nuclear Fuels Plc, Sellafield Works, Seascale, Cumbria CA20 1PG (GB).

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(54) Title: SEPARATION OF METALS

(57) Abstract: The invention provides a process for the separation of metals, the metals being comprised as the metal oxides in a mixed oxide sample, the process comprising: (i) adding the mixed oxide to a molten salt electrolyte and cathodically electrolysing the oxide, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of metal from the cations present in the molten salt, and the applied potential difference being such as to facilitate selective reduction of one metal oxide at the expense of other metal oxides; and (ii) separating the metal from the remaining metal oxides, wherein the metal oxides comprise oxides of metals from at least one of the transition metal, lanthanide or actinide series. The process is applicable to mixed oxide samples comprising mixtures of two or more metal oxides, and a particular application is in the separation of zirconium and hafnium comprised in mixed zirconium and hafnium oxides, the removal of hafnium facilitating the use of the zirconium in fuel cladding for use in the nuclear power industry.

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A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C25C3/00 C22B3/00 C22B34/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C25C C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	WO 02/066712 A (BRITISH NUCLEAR FUELS PLC ; PITNER WILLIAM ROBERT (GB); SMART NEIL GRA) 29 August 2002 (2002-08-29) page 10, line 23 - page 11, line 13	1-11
X	US 4 762 694 A (MARONI VICTOR A ET AL) 9 August 1988 (1988-08-09) claim 1; example 1	1
Y	US 4 923 577 A (MC LAUGHLIN DAVID F ET AL) 8 May 1990 (1990-05-08) column 2, line 44 - column 4, line 22 ----- -/-	3

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

/GB 03/05238

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